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Non-cyclopentadienyl zirconium complexes as catalysts for 1-hexene polymerization

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Abstract

The new β -diketonate complexes (hfac)₂ZrCl₂, (hfac)₃ZrCl, hfac = hexafluoroacetylacetonate, and (thd)₂ZrCl₂, thd = 2,2,6,6-tetramethyl-3,5-heptanedionate, have been prepared in good yield by reacting the corresponding β -diketonate thallium complexes with ZrCl₄ in stoichiometric amounts and they have been characterized by elemental analyses and NMR spectra.

These complexes and the β -diketonate complexes (acac)₂ZrCl₂, (acac)₃ZrCl and (thd)₃ZrCl have been tested as catalysts in the polymerization of 1-hexene in the presence of *N*,*N*'-(dimethylanilinium)-tetrakis(pentafluorophenylborate) or ethyltrichloroacetate as co-catalysts at room temperature using ethyl aluminum sesquichloride as scavenger. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Non-cyclopentadienyl catalysts for the olefin polymerization field are a well defined challenge coming partly from the need of bypassing the growing set of patents in group 4 cyclopentadienyl systems and the need of exploring alternative metal-based catalyst systems [1].

The development of these new catalyst systems is based on the use of new metals such as the group 10 metals or/and the introduction of nitrogen as well as oxygen-based ligands.

In particular, group 4 metal complexes containing amidic ligands resulted to be promising catalysts for olefin polymerization [1,2].

Recently, we have prepared the η^2 -formamidinyl Zr complexes $Zr X_2[C(NAr)NMeCvc]_2$, (Ar = 2,6-

dimethylphenyl; Cyc = cyclohexyl; X = Cl, OC_6F_5 , NMeCyc) [3] upon double insertion of isocyanides into Zr–N amido bond of Zr-tetraamides and tested them as catalysts in the polymerization of ethylene and 1-hexene. Their activity resulted in low to moderate production of polymers with interesting rheological properties and high molecular weights with low dispersivity.

These results have prompted us to extend our research to Zr complexes containing also oxygenbased ligands. Some oxygen-based ligands have been used to form electronically unsaturated early transition metal complexes with more or less remarkable effects [4].

Our attention was therefore focused on zirconiumchelate complexes containing β -diketonate ligands. The presence of two or more *bis*-chelate ligands may determine different chiral forms of the compounds [5] which is a prerequisite for the stereoregular coordination polymerization of prochiral α -olefins [6–14].

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In the literature, it has been already reported the study of acetylacetonate zirconium $L_{4-n}ZrCl_n$, (L = acetylacetonate, n = 0,1,2)-methylalumoxane systems as soluble Ziegler–Natta olefin polymerization catalysts in particular of the polymerization of ethene [15].

Therefore, we decided to investigate the catalytic behavior of zirconium-based complexes of general formula L_nZrCl_{4-n} (L = acetylacetonate (acac), 2,2,6,6-tetramethyl-3,5-heptanedionate (thd), hexafluor-oacetylacetonate (hfac), with n = 2 or 3) in the polymerization of 1-hexene using as co-catalyst the more stable N,N'-dimethylanilinium-tetrakis(pentafluorophenylborate) or ethyltrichloroacetate, also less expensive than methylalumoxane (MAO).

Here, we report the synthesis and characterization of the Zr complexes and the results of their application as catalysts in the polymerization of 1-hexene. The catalytic activities of the Zr complexes have been compared with those obtained under the same conditions by using the catalyst Cp_2ZrCl_2 as reference.

2. Results and discussion

2.1. Synthesis and characterization of the β -diketonate complexes

In our previous work [3], the synthesized η^2 -formamidinyl Zr complexes resulted to be highly oxygen and moisture sensitive complexes, which require reaction conditions and manipulations in severely controlled inert atmosphere.

With the aim to obtain less sensitive catalysts and to test different co-catalysts as activators, we prepared a series of zirconium β -diketonate derivatives: namely the acetylacetonate complexes (acac)₂ZrCl₂ **1** and (acac)₃ZrCl **2** [16], the hexafluoroacetylacetonate derivatives (hfac)₂ZrCl₂ **3** and (hfac)₃ZrCl **4** and the 2,2,6,6-tetramethyl-3,5-heptanedionate complexes (thd)₂ZrCl₂ **5** and (thd)₃ZrCl **6** [17].

Complexes 3, 4 and 5 were obtained by reacting TIX (X = hfac, thd) with the stoichiometric amount of $ZrCl_4$ in Et₂O (Scheme 1) as white powders after filtration of the precipitated TICl and drying under vacuum.



Scheme 1.

The complexes have been characterized by elemental analysis and ¹H NMR.

The ¹H NMR spectra in CDCl₃ are quite simple: in the case of the hfac complexes the signal of the CH proton is a singlet at 6.58 ppm, the same value for both complexes indicating no particular effect of the coordination of two or three hfac molecules to the zirconium center on the resonance, thus suggesting highly symmetric molecules.

In the case of **5**, the signals of the methyl and CH protons are singlets at 1.17 and 5.99 ppm, respectively, while the signals of the corresponding protons in Tl(thd) fall at 1.14 and 5.57 ppm, and the observed shift could be mainly due to the coordination to different metal centers.

2.2. Polymerization of 1-hexene

In a previous paper [15], it has been reported that acetylacetonate and dibenzoylmethanate Zr complexes were used as catalysts of the polymerization of ethylene in the presence of MAO as co-catalyst: they showed moderate activity and produced polymers with higher molecular weight than those obtained with Cp_2ZrCl_2 under the same conditions, indicating the relevant role of the steric hindrance of the chelate ligand in the polymerization process. However, the high molar ratios Al:Zr employed (4000:1) are an unfavorable characteristic of these complexes.

On this basis, we investigated the behavior of some other zirconium β -diketonate complexes as catalysts in the polymerization of 1-hexene by using as co-catalysts N,N'-dimethylanilinium-tetrakis(pentafluorophenylborate) or ethyltrichloroacetate in comparison with the zirconium acetylacetonates **1** and **2** and the metallocene Cp₂ZrCl₂.

While the co-catalyst N,N'-dimethylanilinium-tetrakis(pentafluorophenylborate) has been widely used in olefin polymerizations, here we report the first application of a polyhalogenated organic compound, ethyltrichloroacetate, as co-catalyst in the polymerization of olefins catalyzed by zirconium complexes. The use of polyhalo-activators in the polymerization of olefins has been already reported in the late 1960s [18] and since then esters of acetic trichloro acid appeared to be the preferred promoters with vanadium complexes [19].

The polymerization results are presented in Table 1.

The system obtained by the combination of such complexes with N,N'-(dimethylanilinium)-tetrakis(pentafluorophenylborate) or ethyltrichloroacetate and ethyl aluminium sesquichloride (EASC) catalyzed the polymerization of 1-hexene under mild reaction conditions although with low activity, comparable with that of Cp₂ZrCl₂ under the same conditions.

The activity of the complexes in the presence of N,N'-(dimethylanilinium)-tetrakis(pentafluorophenylborate)

Table 1				
Conditions and	results of	the polyme	rization of	1-hexene

Catalyst (0.05 mmol)	Co-catalyst										
	<i>N</i> , <i>N</i> '-(dimethylanilinium)- tetrakis(pentafluorophenylborate) (0.05 mmol)				Trichloroethylacetate (0.7 mmol)						
	T _{in} ^a (°C)	$T_{\rm fin}^{\ b}$ (°C)	Activity ^c	1-hexene conversion (%)	PM (g/mol)	T_{in}^{a} (°C)	T_{fin}^{b} (°C)	Activity ^c	1-hexene conversion (%)	PM (g/mol)	
$(acac)_2 ZrCl_2$ (1)	24	29	3.6	0.90	9178	20	22	2.9	0.73	2180	
$(acac)_3 ZrCl(2)$	25	29	6.3	1.54	1151	19	22	3.9	0.97	872	
$(hfac)_2 ZrCl_2$ (3)	29	32	5.2	1.30	18476	22	24	4.2	1.06	32578	
(hfac) ₃ ZrCl (4)	26	29	7.0	1.76	6907	23	28	5.3	1.29	15406	
$(thd)_2 ZrCl_2$ (5)	26	29	7.7	1.92	3380	21	23	4.9	1.02	1558	
$(\text{thd})_3$ ZrCl (6)	25	27	7.3	1.82	2205	21	24	4.3	1.09	820	
$Cp_2ZrCl_2^d$ (7)	26	29	7.6	1.85	6614	25	27	4.3	1.12	1112	

^a $T_{\rm in}$, initial temperature.

^b T_{fin} , final temperature.

^c Activity in K g_{pol}/mol_{cat} h bar.

^d Standard metallocene catalyst as reference.

was higher than by using ethyltrichloroacetate as promoter. However, this is the first example of the application of polyhalogenated organic compound in the polymerization of olefins catalyzed by zirconium complexes.

While in the case of N,N'-(dimethylanilinium)-tetrakis(pentafluorophenylborate), it could be possible to suggest that the polymerization can be favored by a certain degree of protonation of the β -diketonate ligand, thus increasing the Lewis acidity of the zirconium ion, in the case of ethyltrichloroacetate, at the moment, we are unable to explain this activity even though we verified that the co-catalyst plays an important role as in its absence the polymerization did not occur.

In the polymerizations carried out with N,N'-(dimethylanilinium)-tetrakis(pentafluorophenylborate) as co-catalyst, the tetramethylheptanedionates 5 and 6 showed the highest activities and the higher 1-hexene conversions, even though the obtained polymers showed lower molecular weights than those obtained with the hexafluoroacetylacetonates 3 and 4. The less steric hindrance of the hexafluoroacetylacetonate ligand with respect to the tetramethylheptanedionate may justify the higher molecular weights of the polymers as the more crowded thd ligands favor the termination reactions, while the inductive effects of the fluorine atoms in the hfac complexes may be responsible of the relatively high activities of these complexes. As a confirmation, it must be noted that the molecular weights of the polymers obtained from precursors of general formula L₃ZrCl (2, 4, 6) are lower than those obtained from precursors of general formula L_2ZrCl_2 (1, 3, 5).

That the steric hindrance of the ligands plays a prevailing role with respect to the inductive effects has been shown in the polymerizations catalyzed by the thd complexes 5 and 6 with both co-catalysts. In fact the chelate 5, containing two thd ligands, is more active than 6 with three thd ligands. On the other hand, by comparison of the activities between the complexes containing two chelating ligand and those containing three ligands the higher activities of L_3ZrCl species (2, 4) with respect to those of the L_2ZrCl_2 species (1, 3) could be reasonably due to the different geometries of the complexes.

All the polymers obtained showed low molecular weights and the polymers with the highest molecular weights were obtained with complex 3 in the presence of both co-catalysts.

3. Conclusions

The new β -diketonate complexes **3**, **4** and **6** have been easily prepared in good yield by reacting the corresponding β -diketonate thallium complexes with ZrCl₄ in stoichiometric amount.

Complexes 1–7 catalyzed the polymerization of 1-hexene in the presence of N,N'-(dimethylanilinium)-tetrakis(pentafluorophenylborate) or ethyltrichloroace-tate as co-catalyst under mild conditions, although with low activity and producing polymers with low molecular weights. A poly-halogenated organic compound has been proven for the first time to promote the polymerization of 1-hexene with Zr complexes in the presence of EASC and this may open a new interesting field in the research of co-catalysts more easily to be handled, stable and less expensive than MAO.

4. Experimental

4.1. Reagents and physical measurements

Manipulations were performed in an oxygen and moisture-free atmosphere in a Braun MB 200 G-II dry-box. All the solvents were purified and dried following standard procedures [20]. ZrCl₄ (Aldrich), TlOEt 98% (Aldrich), hexafluoroacetylacetone (Aldrich), 2,2,6,6-tetramethyl-3,5-heptanedione 98%, ethyltrichloroacetate (Fluka), [HNMe₂Ph]B(C₆F₅)₄ (Montell) and ethyl aluminum sesquichloride EASC (Albermarle) were used as received. Acetylacetone was distilled before use, 1-hexene (Aldrich) was fractionally distilled on CaH₂ and kept on molecular sieves (NaA zeolites, 8-12 mesh). Complexes (acac)₂ZrCl₂, (acac)₃ZrCl and (thd)₃ZrCl were synthesized according to methods reported in reference [16] and [17], respectively. Tl(hfac) was prepared from TlOEt and hexafluoroacetylone analogously to the synthesis of Tl(thd) reported below. Microanalyses were carried out at Istituto di Chimica Inorganica e delle Superfici, CNR, Padova. The ¹H and ¹³C NMR spectra were obtained as CDCl₃ solutions on a Bruker AMX-300 spectrometer operating at 300 and 75.48 MHz respectively. The assignments of the proton and carbon resonances were performed by standard chemical shift. The determination of the average molecular weight of the polymer was carried out on a Hubbehold viscometer in toluene solutions at 55 °C.

4.2. Polymerization of 1-hexene

In a three-neck round bottom flask, 1-hexene (20.19 g), EASC (4×10^{-4} mol) and a solution of the complex (5×10^{-2} mmol) and co-catalyst in toluene (200 ml) were introduced. The reaction was carried out at room temperature for 1 h at 1.003 bar.

After adding MeOH (1 or 2 ml) at the end of the reaction, the reaction solution was evaporated under reduced pressure and the polymer was dried at 60–70 °C under vacuum. The polymer (0.5 g) was dissolved in toluene (50–60 ml) and the solution washed three times with a solution of MeOH–HCl 1:1 (3×50 ml). The addition of a MeOH–acetone solution 1:1 (50 ml) and shaking vigorously caused the coagulation of the polymer which was separated and dried at 90 °C for 3 h under vacuum.

4.3. *Tl(thd)*

To a solution of 2,2,6,6-tetramethyl-3,5-heptanedione (2.947, 15.7 mmol) in *n*-pentane (10 ml) TlOEt (3.698 g, 14.5 mmol) was added. After stirring overnight, the solution was evaporated to dryness under vacuum obtaining Tl(thd) as a white solid in quantitative yield (5.62 g). Elemental *Anal*. Calc. for C₁₁H₁₉O₂Tl requires C, 34.06; H, 4.10. Found: C, 34.18; H, 4.12%. ¹H NMR (CDCl₃, δ , ppm): 1.130 (*CH*₃), 5.554 (*CH*). ¹³C (CDCl₃, δ , ppm): 28.70 (*C*H₃), 91.32 (*C*H).

4.4. $(hfac)_2 Zr Cl_2$ (3)

Solid $ZrCl_4$ (0.620 g, 2.6 mmol) was slowly added to a solution of Tl(hfac) (2.14 g, 5.2 mmol) in Et₂O (10 ml)

under stirring. The precipitation of TlCl as a white solid occurred immediately. After stirring overnight, the mixture was filtered and the filtrate evaporated to dryness under vacuum. The white residue was washed with a small amount of Et₂O and dried under vacuum. Yield: 1.019 g, 68%. Elemental *Anal*. Calc. for C₁₀H₂Cl₂O₄Zr requires C, 20.84; H, 0.17. Found: C, 20.23; the H percentage has not been determined because the signal is covered by the noise of the instrument. ¹H NMR (CDCl₃, δ , ppm): 6.584 (CH). ¹³C (CDCl₃, δ , ppm): 95.10 (*C*H).

4.5. $(hfac)_{3}ZrCl$ (4)

Solid ZrCl₄ (0.47 g, 2 mmol) was slowly added to a solution of Tl(hfac) (2.530 g, 6.1 mmol) in Et₂O (10 ml) under stirring. The precipitation of TlCl as a white solid occurred immediately. After stirring for 2 h, the mixture was filtered and the filtrate evaporated to dryness under vacuum. The white residue was washed with a small amount of Et₂O and dried under vacuum. Yield: 1.030 g, 68%. Elemental *Anal*. Calc. for C₁₅H₃ClO₆Zr requires C, 24.09; H, 0.13. Found: C, 24.15; the H percentage has not been determined because the signal is covered by the noise of the instrument. ¹H NMR (CDCl₃, δ , ppm): 6.582 (CH). ¹³C (CDCl₃, δ , ppm): 95.13 (CH).

4.6. $(thd)_2 ZrCl_2$ (5)

Solid ZrCl₄ (0.443 g, 1.9 mmol) was slowly added to a solution of Tl(thd) (0.150 g, 3.8 mmol) in Et₂O (10 ml) under stirring. The precipitation of TlCl as a white solid occurred immediately. After stirring for one night, the mixture was filtered and the filtrate evaporated to dryness under vacuum. The white residue was washed with a small amount of Et₂O and dried under vacuum. Yield: 0.760, 76%. Elemental *Anal.* Calc. for C₂₂H₃₈Cl₂O₄Zr requires C, 52.29; H, 7.47. Found: C, 52,35; H, 7.49%. ¹H NMR (CDCl₃, δ , ppm): 1.166 (CH₃), 5.992 (CH). ¹³C (CDCl₃, δ , ppm): 27.9 (CH₃), 94.0 (CH).

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